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# One-step production of 1,3-butadiene from 2,3-butanediol dehydration

Xi Liu,<sup>[a]</sup> Viktoria Fabos,<sup>[a]</sup> Stuart Taylor,<sup>[a]</sup> David W. Knight,<sup>[a]</sup> Keith Whiston,<sup>[b]</sup> Graham J. Hutchings<sup>\*[a]</sup>

**Abstract:** We report the direct production of 1,3-butadiene from the dehydration of 2,3-butanediol by using alumina as a catalyst. Under optimized kinetic reaction conditions, the production of methyl ethyl ketone and isobutyraldehyde, formed via the pinacol-pinacolone rearrangement, was markedly reduced and over 80% selectivity to 1,3-butadiene and 3-buten-2-ol could be achieved. The presence of water plays a critical role in the inhibition of oligomerization. The amphoteric nature of  $\gamma$ - $\text{Al}_2\text{O}_3$  was identified as important and this contributed to the improved catalytic selectivity when compared with other acidic catalysts.

The use of renewable biomass as a resource for chemical and fuel production has been gaining increasing attention during the last two decades. This is in response to the present global challenge related to the use of fossil fuels and the environmental problems to which their use may contribute. However, installed production capacity based on renewable resources has not reached the levels anticipated due to economic reasons and it has increased at a slower rate than originally forecast.<sup>[1]</sup> One of the key problems is the production of vast amounts of lower value by-products which have limited applications, for instance, glycerol generated from biodiesel production and butanediols generated from biomass fermentation or wood hydrolysis. These by-products potentially make the overall process less efficient and non-profitable.<sup>[2]</sup> Therefore, the development of value-added uses for the crude biomass-derived by-products or the so-called 'biomass waste' will contribute to the viability of the nascent biomass industry.<sup>[3]</sup> Besides the reduction of waste with a reduced impact on the environment, the recovery of energy and useful feedstocks could make these processes economically practical and competitive against present industrial processes based on readily available fossil fuels.

Recent work has revealed the potential of 2,3-butanediol (BDO) as a promising  $\text{C}_4$  platform chemical for use in a variety of industrial applications.<sup>[4, 5]</sup> BDO had been used as the precursor to produce deacetyl, butenes or 1,3 butadiene before the availability of processes based on the ready availability of inexpensive fossil hydrocarbons were introduced in the 1950s. At present, BDO has only limited industrial applications as a food

flavour additive.<sup>[6]</sup> However, the development of the biomass industry and the abundance of BDO as a by-product have reignited interest in the catalytic conversion of BDO, in particular its dehydration to 1,3-butadiene (BDE). At present, attempts to directly produce BDE with a high yield has failed and the reaction to methyl ethyl ketone, the thermodynamically preferred product, always predominates.<sup>[7-9]</sup> The mechanism is well understood since the consecutive dehydration of the adjacent two hydroxyl groups leads to an enol which readily forms methyl ethyl ketone (MEK). To achieve high yields of the required product, a two-step process has been designed to convert the diol into the diene by using an acid as an esterifying agent, or catalytic reductive deoxygenation in the presence of  $\text{H}_2$  has been used.<sup>[10-12]</sup> Both processes are not environmental benign and make industrial production economically less attractive due to usage of either a stoichiometric acid or reductant. In addition, biomass-derived polyols are formed at low concentrations in aqueous solution. Refining these crude aqueous solutions, using distillation or membrane separation, is an endothermic reaction requiring a high-energy input, which also hinders the overall potential catalytic conversion process.<sup>[13, 14]</sup>

Here we report a facile method to produce BDE with almost 100% selectivity via the direct dehydration of aqueous BDO using a commercial alumina catalyst. High selectivity to butadiene is achieved by using high flow rates and a low amount of catalysts. Our work suggests that under these optimised kinetic reaction conditions the consecutive dehydroxylation via 1,2-elimination to BDE by an E2 mechanism is favoured.

The activities for the dehydration of BDO (10 wt%) using a range of catalysts were investigated (Table 1). In most cases, by using a relatively large amount of catalyst (0.5 g), the major product was always MEK, which was produced via partial dehydration followed by the pinacol-pinacolone rearrangement (equations 1-5).<sup>[15]</sup> The major by-product was isobutyraldehyde (IBA), which was also generated via the pinacol-pinacolone rearrangement (equations 1, 2, 6-9). BDE was only observed as a minor product for almost all catalysts, except  $\gamma$ - $\text{Al}_2\text{O}_3$ , where BDE selectivity was 21% at 350 °C (Table 1, entry 13). This was almost double the selectivity observed using bentonite and  $\text{SiO}_2$  under the identical conditions (Table 1, entries 3 and 5). Compared to  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\alpha$ - $\text{Al}_2\text{O}_3$  showed lower productivity of BDE and much higher productivity of IBA at 350 °C (Table 1, entry 11). At a lower temperature (260 °C), the selectivity to BDE when using  $\gamma$ - $\text{Al}_2\text{O}_3$  decreased markedly to 7% at almost complete conversion. At 260 °C, we investigated the influence of the BDO concentration on the catalytic performance of  $\gamma$ - $\text{Al}_2\text{O}_3$  and complete conversion of BDO was always observed (Table 2). However, the use of 100% BDO does not favour the overall catalytic performance as a low carbon balance was observed (Table 2, entry 1), which could be attributed to the production of di- and tri- oligomers which remained on the catalyst. Addition of

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a small amount of water (5 wt%) significantly improved the carbon balance from 86% to 96% (Table 2, entry 2). No loss in carbon balance was observed upon further dilution even with high levels of water (i.e. 10 wt% BDO). This confirmed that the presence of water was key for the inhibition of oligomerization.<sup>[16]</sup>

The use of alumina as a catalyst for the dehydration of BDO has been reported previously,<sup>[16]</sup> when 42% selectivity to BDE with 100% BDO conversion was obtained in the presence of H<sub>2</sub>. In our case we do not require the presence of H<sub>2</sub> to achieve higher selectivities. Generally, only very limited work can be found over the past 80 years concerning the selective production of BDE from BDO dehydration, apart from the use of thorium in 1945, which has never been used commercially due to the radioactive nature of the catalyst.<sup>[7]</sup> Therefore, there is no previous mechanistic work on the production of BDE via stepwise dehydration of BDO. With other oxides such as MoO<sub>3</sub> and WO<sub>3</sub>, low carbon balances were observed due to the production of cracking products, e.g. propene and propane. This suggests a negative role of redox active catalysts in the dehydration reaction, which could lead to C-C bond fission.

We noted that, even at lower temperature (260 °C), almost 100% conversion could be obtained with Y- Al<sub>2</sub>O<sub>3</sub> (Table 1, entry 14). Clearly this indicated that we were probably using too much catalyst and the reaction was not being operated under kinetic reaction conditions. Hence, we decreased the amount of the catalyst from 500 mg to 3 mg (Table 3, entry 1 to 4). For comparison, we also tested other oxides and acid catalysts under identical conditions. Obviously, the use of lower amounts of the catalysts led to lower conversions of BDO. Simultaneously, the selectivity to BDE increased markedly. This suggested that the presence of diffusion control or strong adsorption/re-adsorption, which could reduce the production of butadiene was present when using large amounts of the catalyst. The best selectivity of 50% to BDE was still obtained by using Y- Al<sub>2</sub>O<sub>3</sub>. The difference in catalytic performance between Y- Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> was also observed; while the former favoured production of BDE and MEK, the latter produced MEK, BDE, as well as IBA. This suggests that moderate acidity is the key factor for the selective dehydration of BDO. Reproducibility of the catalytic performance of Y- Al<sub>2</sub>O<sub>3</sub> was also investigated which confirms low variability in the results using three independent tests (Table 4),

To reduce the re-adsorption and diffusion-control, we adjusted the contact times by changing the carrier gas flow rate from 15 mL/min to 300 mL/min under the same reaction conditions using 3 mg Y- Al<sub>2</sub>O<sub>3</sub> (Table 5 entry 1 to 9, and Figure 1). At the lowest flow rate, ca. 50% conversion of BDO was observed but with only 10% selectivity to BDE. As the flow rate was increased to 150 mL/min, the selectivity to BDE increased to 60% and the conversion decreased to 18%. However, with the highest flow rate, the selectivity to BDE did not increase, but decreased to 40% with the production of 3-buten-2-ol (BTO). No production of MEK was observed with the highest flow rate of 300 mL/min. This suggested that the production of BDE came from further dehydration of BTO, generated via a  $\beta$ -hydride elimination from the terminal methyl group. In this case, production of MEK via the pinacol-pinacolone rearrangement decreased with higher flow rate. It suggests strong dependence of BDE and MEK on the

flow rate should be associated with different reaction pathways. Moreover, we found that the higher flow rates also favoured the production of BDE by using other catalysts, e.g.  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> and silica tungstic acid. This suggests that this is general trend, correlated with the production of BDE via a consecutive two-step dihydroxylation process (Scheme 1), which can be catalysed by the acidic active sites in these catalysts. However, the stronger acidity of silicotungstic acid does not favour the production of BDE,<sup>[17]</sup> which suggests moderate acidity is the key requirement for BDE formation. It is possible that stronger acidity leads to the isomerization reactions and the production of MEK and IBA.

Performance of Y- Al<sub>2</sub>O<sub>3</sub> was also studied under the optimised reaction conditions (Figure 2 and Table 6). No activity of Y-Al<sub>2</sub>O<sub>3</sub> was observed at 150°C. At low temperatures (200-250°C), IBA is the major product with lower production of BDE and BTO. Once the reaction temperature was increased to 300°C, the selectivity to IBA decreased from 78% to 21%, whilst the conversion of BDO simultaneously increased from 2% to 8%. The catalytic performance of Y- Al<sub>2</sub>O<sub>3</sub> was quite stable at reaction temperatures ranging from 300 to 350°C, while no production of MEK was detected. However, at the higher temperature, production of MEK was observed and increased as a function of reaction temperature. It is suggested that, production of IBA and MEK via the pinacol-pinacolone rearrangement may occur under different reaction conditions with the latter product favoured by higher reaction temperature. The results also suggested that the carbonium ion (Equation 2) formed via acid-catalyzed extraction of the OH group, might be the key intermediate for the generation of IBA, BTO, BDE and MEK (Scheme 1). Strong acidity or higher temperatures favour the production of MEK due to either strong adsorption on the catalyst or instability of the intermediate at the higher temperature. Weaker adsorption assigned to moderate acidity and decreased re-adsorption could promote the stepwise elimination of hydroxyl groups, which improved the production of BDE.

Dehydration of 3-buten-2-ol by using Y- Al<sub>2</sub>O<sub>3</sub> was tested under similar reaction conditions (10 wt% BTO in water, 0.02 mL/min, 3 mg catalysts, 300 mL/min Ar, Table 7) to those used previously for BDO. Almost complete transformation of BTO to BDE was observed with only a small amount of IBA being detected in the products. The production of IBA could be attributed to the rearrangement of 3-buten-2-ol or the addition of water to BDE.

In this work, Y- Al<sub>2</sub>O<sub>3</sub> has been confirmed as a catalyst for the direct dehydration of BDO to BDE, a valuable monomer for production of synthetic rubber. By using trace amounts of catalyst and a high flow rate in a fixed bed reactor, 10% BDO conversion could be achieved with > 80% selectivity to BDE and BTO. The presence of water was found to efficiently improved the overall catalytic performance by reducing oligomerization of BDE.

## Experimental Section



Catalysts, including  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (99.8% trace metal basis, N<sub>2</sub> BET surface area, 1 m<sup>2</sup>/g) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (99.8% trace metal basis, N<sub>2</sub> BET surface area, 105 m<sup>2</sup>/g) were purchased from Sigma Aldrich and used as received. silica tungstic acid obtained from Johnson Matthey. Catalytic dehydration was conducted by using laboratory fixed bed reactor equipped with vaporiser. 2,3-Butanediol (BDO, 10 wt% aqueous solution) was pumped into the middle of the vaporiser with flow rate of 0.02 mL/min where it was vaporized in a flow of argon carrier gas and fed to the catalyst. The temperature of the vaporiser was set as same as reaction temperature. All of the catalysts were pressed and sieved to a uniform particle size distribution of 600-800  $\mu$ m before use and were packed into a 0.8 mm i.d. stainless steel reactor between plugs of quartz wool. Catalyst amounts ranged from 3-500 mg. A glass collection vessel filled with distilled water was connected to the end of the reactor, which was cooled with ice-water, and then gaseous products were collected in a gas bag.

For the first hour of the reaction the products were expelled through a vent and the product collection was started only from the second hour onwards to maximize the mass balance recovery of the products by giving enough time to achieve a proper balance of substrate/water vapour in the reactor. Then the reaction products were collected in cold traps filled with a known amount of distilled water. Two traps were used to ensure that any carry-over from the first trap was collected in the subsequent trap (however, most of the cases, no products were observed in the second trap). The gas phase was collected in a gas sampling bag and analysed offline by gas chromatography. The contents of the traps were worked-up and also analysed by gas chromatography.

The product work-up procedure and analysis as follows. After addition of a known amount of propanol, as an internal standard to the traps, 0.75 ml aqueous solution were added to dichloromethane (1-2 mL) which was then dried over sodium sulphate. After filtration the samples were analysed by Varian 430-GC gas chromatograph equipped with a capillary column (Restek, Stabilwax, id 0.25 mm x 15m). Quantification was achieved through a calibration against five different concentrations of authentic samples using propanol as an internal standard, for all products. The injector and detector ports were maintained at 250 °C and the oven was programmed from 40 °C to 200 °C at a rate of 30 °C/min after 3 min waiting at the initial temperature of 40 °C. The column temperature was kept at 200 °C for an additional 2 min. Gas phase analysis was performed using the same gas chromatograph and column, applying a constant temperature program (35 °C) for 8 min. The peak of the BDE can be readily distinguished from propene. Quantification of BDE was achieved through a calibration against five different concentrations, made by controlling the

flow rates of inert argon gas and BDE. Possible production of CO and CO<sub>2</sub> was analysed by a Varian 450-GC gas chromatograph equipped with FID & TCD detectors, a methaniser and a CP-SiL5CB column (50m, 0.33mm diameter, He carrier gas). The qualitative production of the butadiene has been also confirmed by GC-MS.

## Acknowledgements

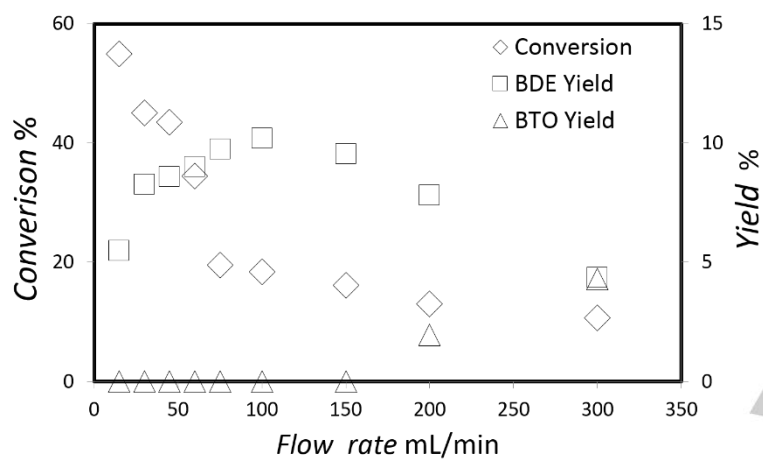
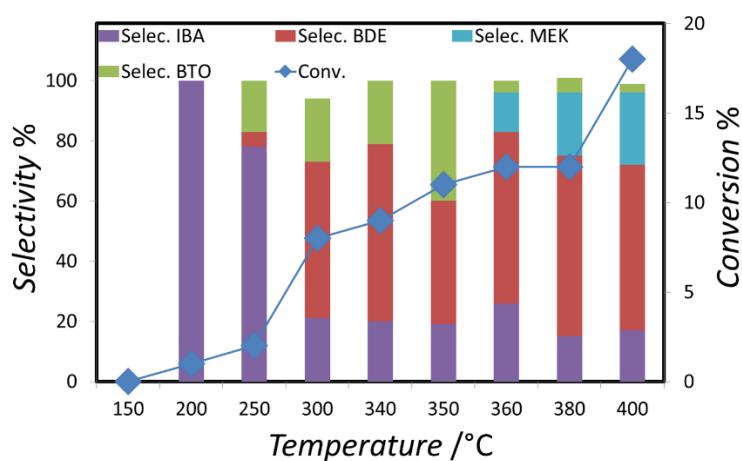
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**Keywords:** 2,3-Butanediol • 1,3-Butadiene • alumina • dehydration

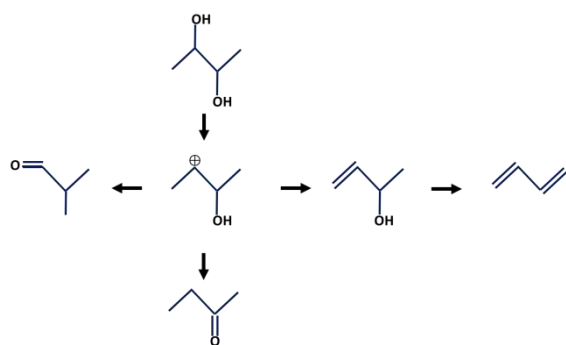
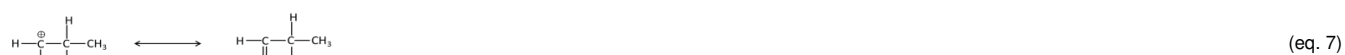
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## Entry for the Table of Contents (Please choose one layout)

Layout 1:

Figure 1. Catalytic activity of Y-Al<sub>2</sub>O<sub>3</sub> as a function of flow rateFigure 2. Catalytic activity of Y-Al<sub>2</sub>O<sub>3</sub> as a function of reaction temperature.

## COMMUNICATION



**Scheme 1.** Methyl ethyl ketone, isobutyraldehyde and 1,3-butadiene derived in the dehydration of 2,3-butanediol

**Table 1.** Catalytic performance of various oxides catalysts

	Catalyst	Temp. °C	Conv. %	Selec. %					Carbon balance %
				BDE	IBA	MEK	BTO	Enenol	
1	SiWO/SiO <sub>2</sub>	350	100	3.7	5.1	91.1	-	-	98
2		260	95	0.5	10	89	-	-	80
3	SiO <sub>2</sub>	350	95	13	17	70	-	-	100
4		260	94	6.4	12	81	-	-	95
5	Bentonite	350	95	13	17	70	-	-	99
6		260	60	2.5	14	77	7.5	-	102
7	CeO <sub>2</sub>	350	94	1.1	15	84	-	-	100
8	SAB-6	350	98	7	9	84	-	-	75
9	MoO <sub>3</sub>	350	98	3.8	8	74	6	7	75
10	WO <sub>3</sub>	350	86	2	12	80	3	2	80
11	α-Al <sub>2</sub> O <sub>3</sub>	350	97	18	12	70	-	-	100
12		260	34	7.9	-	83	-	-	100
13	γ-Al <sub>2</sub> O <sub>3</sub>	350	99	21	3	73	-	-	97
14		260	99	7	5	80	4	4	96
15	Quartz wool	350	0.1	-	45	55	-	-	100
16	SiC	350	0	-	-	-	-	-	-
17	Graphite	350	0	-	-	-	-	-	-

Reaction conditions: 10 wt% BDO, 0.02mL/min; 75 mL/min Ar, catalysts (500 mg), BDE, IBA, MEK, BTO and Enenol represent 1,3-butadiene, isobutyraldehyde, methyl ethyl ketone, 3-buten-2-ol and other butenols (2-buten-1-ol and 3-buten-1-ol), respectively.

**Table 2.** Catalytic performance of γ-Al<sub>2</sub>O<sub>3</sub> at different BDO concentrations

Catalysts	Conc. %	Conv. %	Selec. %					Carbon balance %
			BDE	IBA	MEK	BTO	Enenol	
γ-Al <sub>2</sub> O <sub>3</sub>	100	96	4	4	90	2	-	87
	95	99	5	4	89	2	-	96
	50	100	7	3	89	0	0	100
	10	99	7	5	80	4	4	96

Reaction conditions: 10 wt% BDO, 0.02mL/min; 75 mL/min Ar, catalyst (500 mg)

## COMMUNICATION

**Table 3.** Catalytic activities of oxides and acid catalyst with different catalyst amount

	Catalyst	Mass mg	Conv. %	Selec. %					Carbon balance %
				BDE	IBA	MEK	BTO	Enenol	
1	Y-Al <sub>2</sub> O <sub>3</sub>	500	99	21	3	73	-	-	97
2		40	100	22	13	65	-	-	100
3		6	35	36	23	46	-	-	100
4		3	20	50		47	-	-	98
5	SiO <sub>2</sub>	500	100	3.7	5.1	91.1	-	-	98
6		40	100	16.7	14	69	-	-	100
7		10	23	17		82	-	-	98
8		3	6	21	30	49	-	-	99
9	SiWO	500	100	3	6	89	-	-	97
10		40	90	6	36	55	-	-	97
11		3	14	10	30	60	-	-	98
12	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	500	97	17	12	69	-	-	100
13		5	67	23	9	67	-	-	95
14		3	25	26	24	50	-	-	99

Reaction conditions: 10 wt% BDO, 0.02mL/min; 75 mL/min Ar, 350°C

**Table 4.** Catalytic performance of different batches of Y-Al<sub>2</sub>O<sub>3</sub>

Catalyst	batch	Conv. %	Sel. %					Mass Balance %
			BDE	IBA	MEK	BTO	Enenol	
Y-Al <sub>2</sub> O <sub>3</sub>	1	20	50		47		-	98
	2	19	53		47		-	96
	3	21	52		48		-	100
blank	1	0	0		-		-	101
	2	0	0		-		-	100
	3	0	0		-		-	100
SiC <sup>[a]</sup>	1	1	1		-		-	99
	2	2	2		-		-	98
	3	1.5	-		-		-	98.5 <sup>[b]</sup>

Reaction conditions: 10 wt% BDO, 0.02mL/min, 75 mL/min Ar, Y-Al<sub>2</sub>O<sub>3</sub> (3mg), 350°C; [a] the whole reactor was filled with SiC; [b] no production of BDE, IBA or other products was observed.**Table 5.** Catalytic performance of various oxides catalysts as function of flow rate

Catalyst	Flow rate mL/min	Conv. %	Sel. %					Carbon Balance %
			BDE	IBA	MEK	BTO	Enenol	
1	Y-Al <sub>2</sub> O <sub>3</sub>	15	54	10	8	81		98
2		30	45	18		81		99
3		45	43	20	20	61		97
4		60	30	35	20	45		97
5		75	20	50		47		98
6		100	18	55	12	32		97
7		150	16	60	11	29		95
8		200	13	60	13	11	15	97
9		300	11	41	19	0	40	96
10	SiWO	75	14	10	30	60		101
11		300	2.2	29	31	36	5	99
12	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	75	25	26	24	50		99
13		300	6	32	34	30	4	98

Reaction conditions: 10 wt% BDO, 0.02mL/min, catalysts (3mg), 350°C

The influence of the reaction temperature on the catalytic

**Table 6.** Catalytic performance of Y-Al<sub>2</sub>O<sub>3</sub> catalysts at different temperatures

Catalysts	Temp. °C	Conv. %	Selec. %					Carbon Balance %
			BDE	IBA	MEK	BTO	Enenol	
1	Y-Al <sub>2</sub> O <sub>3</sub>	150	0	-	-	-	-	-
2		200	1	-	100	-	-	100
3		250	2	5	78	-	17	100
4		300	8	52	21	-	21	99
5		340	9	59	20	-	21	101
6		350	11	41	19	0	40	96
7		360	12	57	26	13	4	98
8		380	12	60	15	21	5	99
9		400	18	55	17	24	3	90 <sup>[a]</sup>

Reaction conditions: 10 wt% BDO, 0.02mL/min, catalysts (3mg), 300 mL/min Ar. [a] mass production of propene

## COMMUNICATION

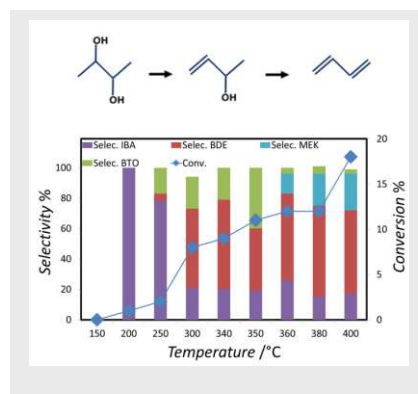
**Table 7.** Catalytic dehydration of BTO

Catalysts	Temp. °C	Conv. %	Selec. %				Carbon Balance %
			BDE	IBA	MEK	Enenol	
Y-Al <sub>2</sub> O <sub>3</sub>	350	94	96	4	-	-	100

Reaction conditions: 10 wt% 3-buten-2-ol in water, 0.02 mL/min, 3 mg catalyst, 300 mL/min Ar.

## COMMUNICATION

Catalytic activity of Y-Al<sub>2</sub>O<sub>3</sub> as a function of reaction temperature



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**One-step production of 1,3-butadiene from 2,3-butanediol dehydration**